Review of Chemical Contaminants in the Sediments of Baltimore Harbor

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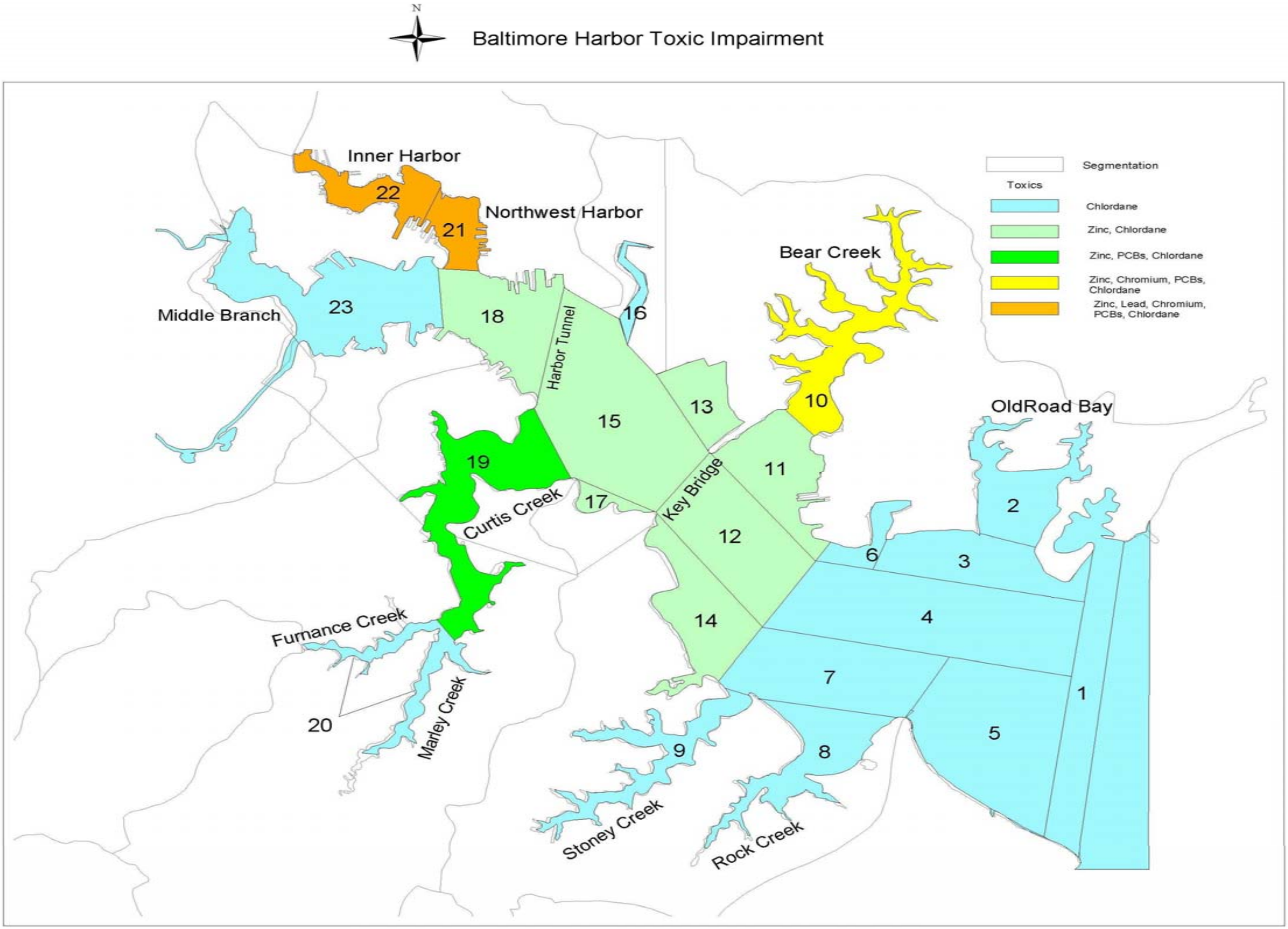
1. Review of field studies
2. Insights from these studies relative to sediment toxicity
3. What do we know about temporal trends in the Harbor?


N
Baltimore Harbor Toxic Impairment
Segmentation
Toxics
Chlordane
Zinc, Chlordane
Zinc, PCBs, Chlordane
Zinc, Chromium, PCBs, Chlordane
Zinc, Lead, Chromium, PCBs, Chlordane
Inner Harbor
Northwest Harbor
Middle Branch
Bear Creek
OldRoad Bay
Harbor Tunnel
Key Bridge
Curtis Creek
Furnance Creek
Marley Creek
Stoney Creek
Rock Creek
1
2
3
4
5
6
7
8
9
10
11
12
13
14
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23

Potential Impairments Due to Contaminated Sediments

- Solid-phase concentration in excess of effects-based endpoints
- Pore-water concentrations in excess of water quality criteria
- Release into overlying water resulting in ambient concentrations in excess of water quality criteria
- Ingestion and accumulation of chemical contaminants in benthic organisms
  - Toxicity
  - Trophic transfer

Potential Confounding Issues

- Seasonal hypoxia/anoxia
  - Benthic habitat degraded
  - Contaminant speciation (bioavailability) altered
- Redox species
  - Toxicity of dissolved sulfide?
  - Toxicity of ammonia?
- Changing sediment toxicity due to sampling and experimental procedures
  - Mixing of more contaminated sediments with the thin layer at the sediment-water interface
  - Oxidation and precipitation of redox metals from the reaeration required for the sediment toxicity testing

Contaminated Sediments: Assessment Strategy

- Phase 1: Initial Assessment
  - Total concentrations in solid phase compared to general benchmarks
  - Acute and chronic sediment toxicity to resident species
- Phase 2: Refined Assessment
  - Further evaluation of ‘hot’ sites
  - Concentration and speciation of stressors in porewaters
  - Statistical analysis: correlations among chemistry and toxicity
- Phase 3: Toxicity Identification and Evaluation
  - Determine ‘most likely’ causative agents
  - Employ newly-developed protocols

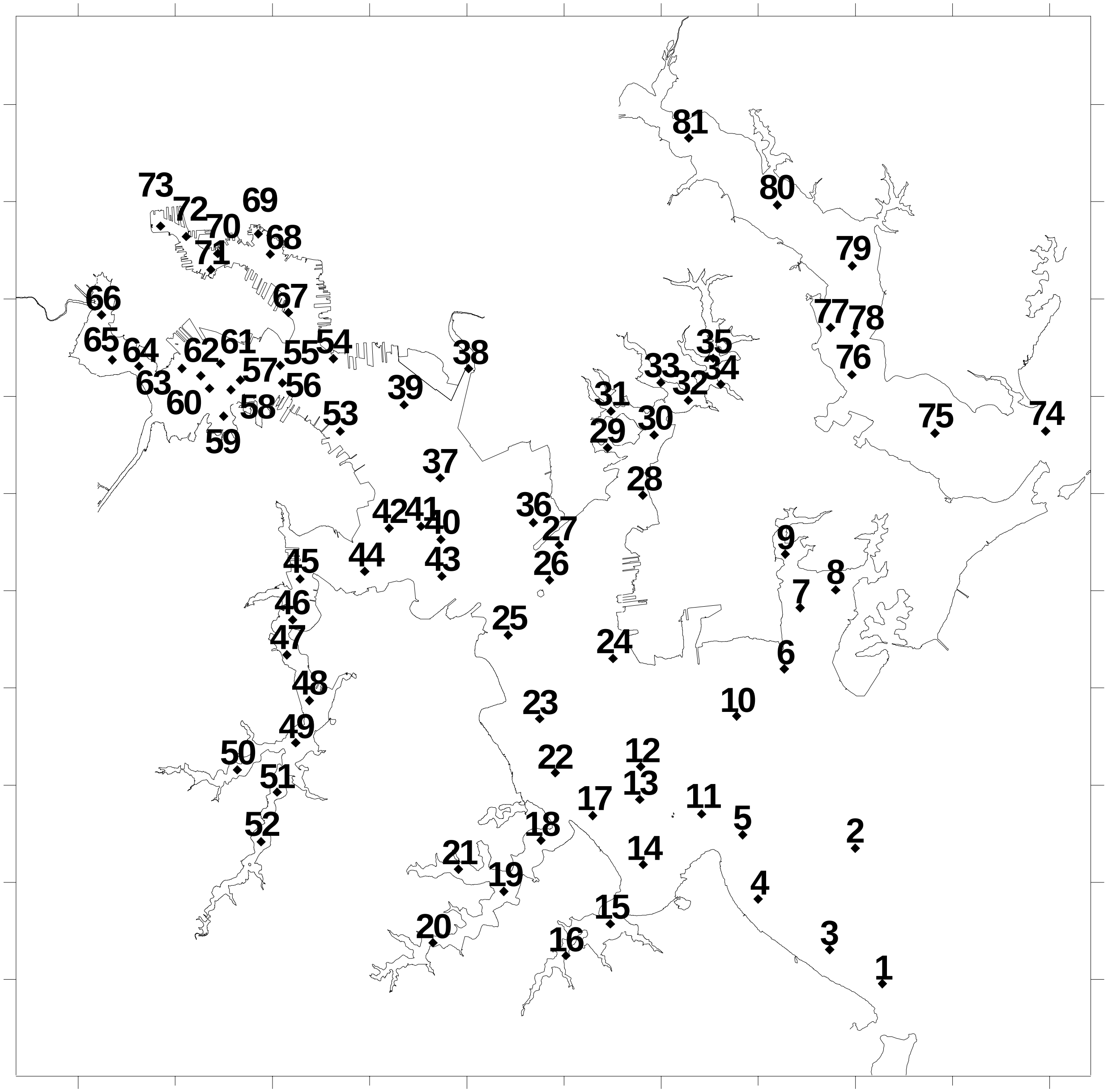
Baltimore Harbor Sediment Studies

1981	•Chromium and zinc in surficial sediments along a harbor-wide transect •Sediment cores at several stations	Sinex, S.A. and G.R Helz (1982) Entrapment of zinc and other trace elements in a rapidly flushed industrial harbor. *Environ. Sci. Technol.*, 16, 820-825
1996	•cadmium, chromium, copper, lead, and zinc •PAHs, PCB congeners, pesticides •72 sites •Surface 2 cm	Ashley, J.T.F. and J.E. Baker (1999) Hydrophobic organic contaminants in surficial sediments of Baltimore Harbor: inventories and sources. *Environ. Toxicol. Chem.*, 18, 838-849. McGee, B.; Fisher, D.J., Yonkos, L.T., Ziegler, G.P., and S. Turley (1999) Assessment of sedimentary contamination, acute toxicity, and population viability of the estuarine amphipod *Leptochirus plumulosis* in Baltimore Harbor. *Environ. Toxicol. Chem.*, 18, 2151–2160

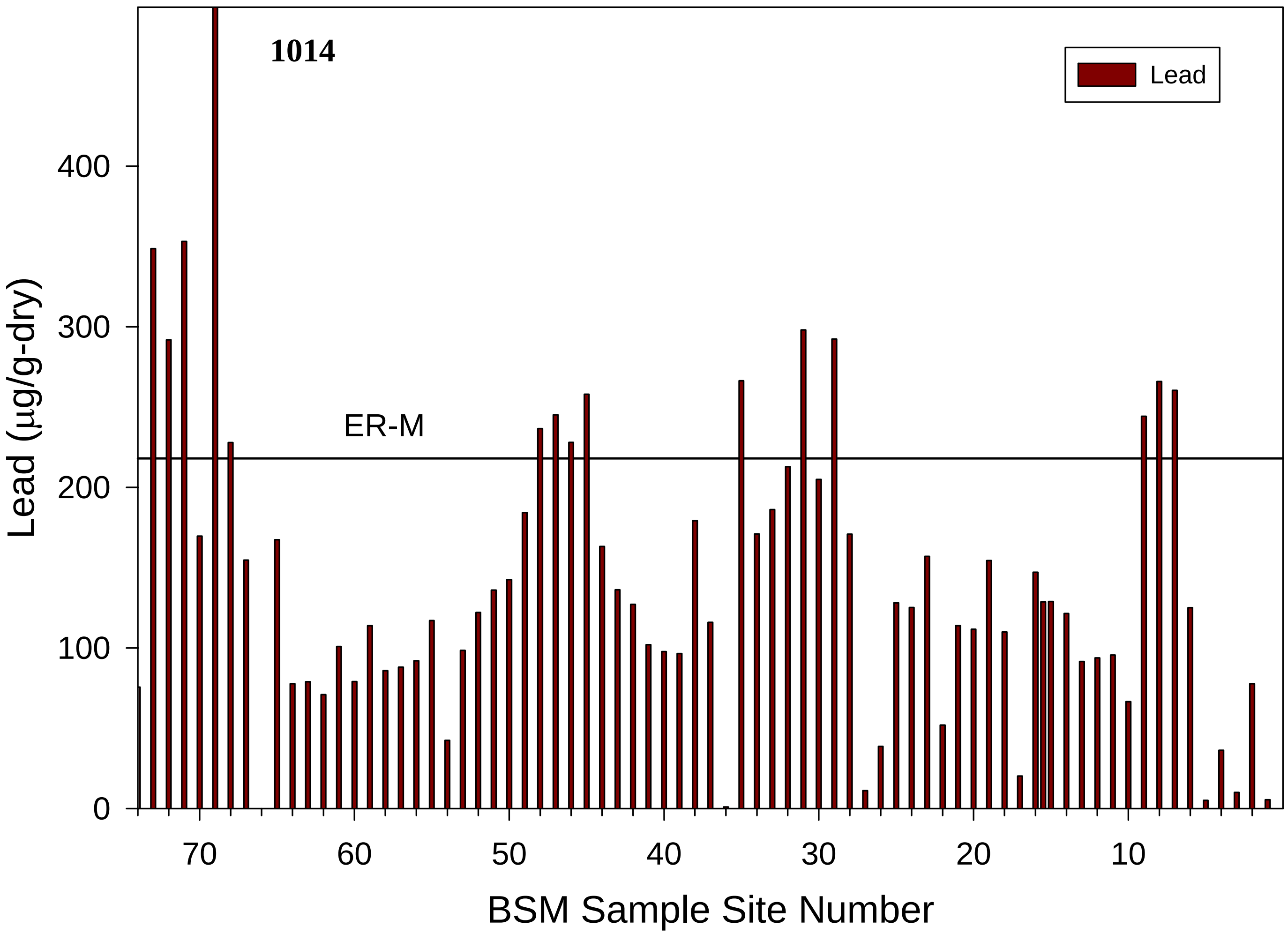
Baltimore Harbor Sediment Studies

1997	•Trace metal geochronologies from three sediment cores	•Mason *et al.*, 2004. Metal accumulation in Baltimore Harbor: Current and Past Inputs •*Applied Geochemistry*, in press
2003	•cadmium, chromium, copper, lead, and zinc •Surficial 2 cm, porewater, AVS/SEM, Cr speciation •Sediment toxicity	•Baker et al., 2003 report to MDE

Baltimore Harbor Sediment Mapping (BSM) Stations



Baltimore Sediment Mapping Results:
Comparison to Effects Range-Median (ER-M) Benchmark



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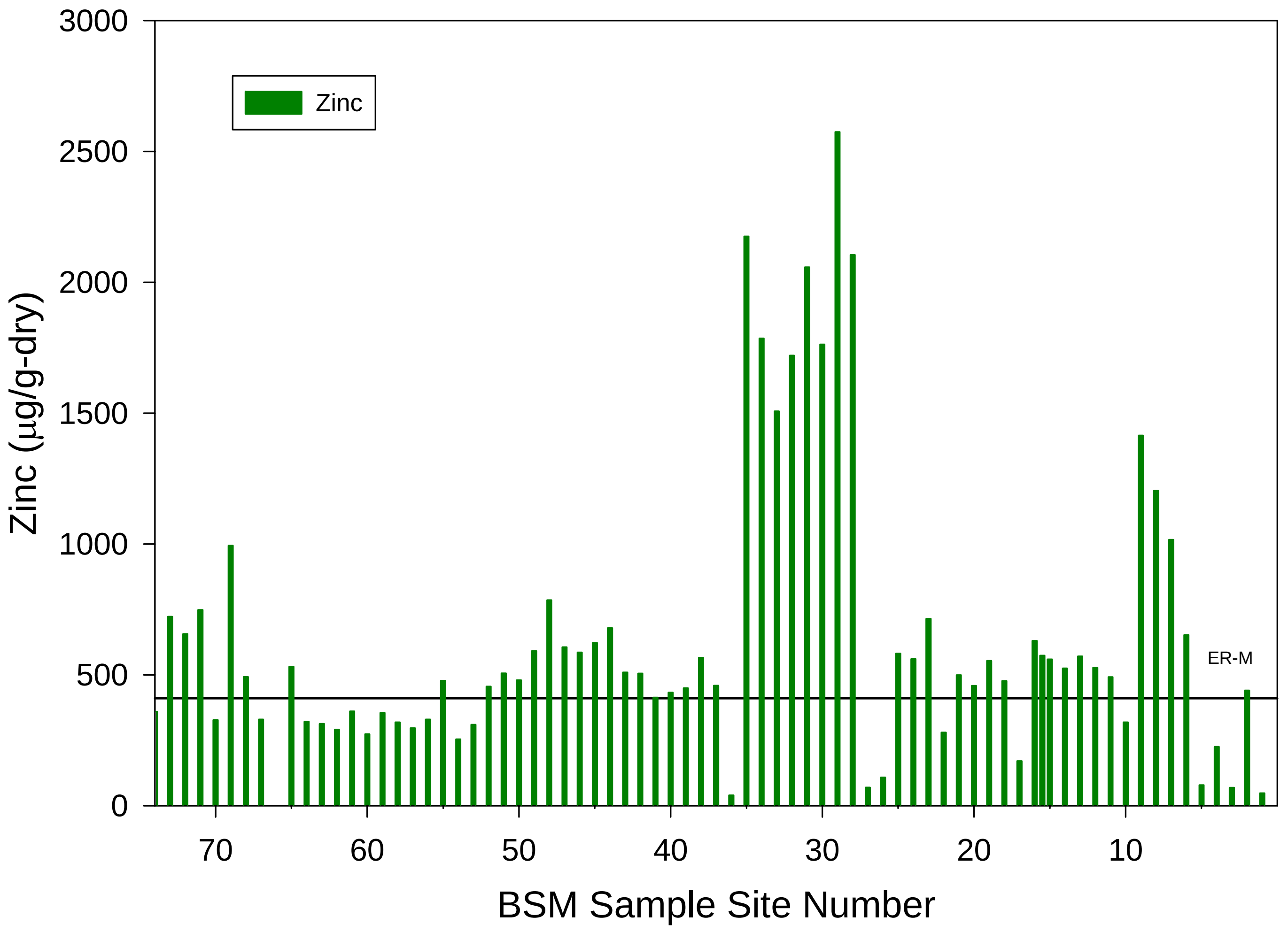

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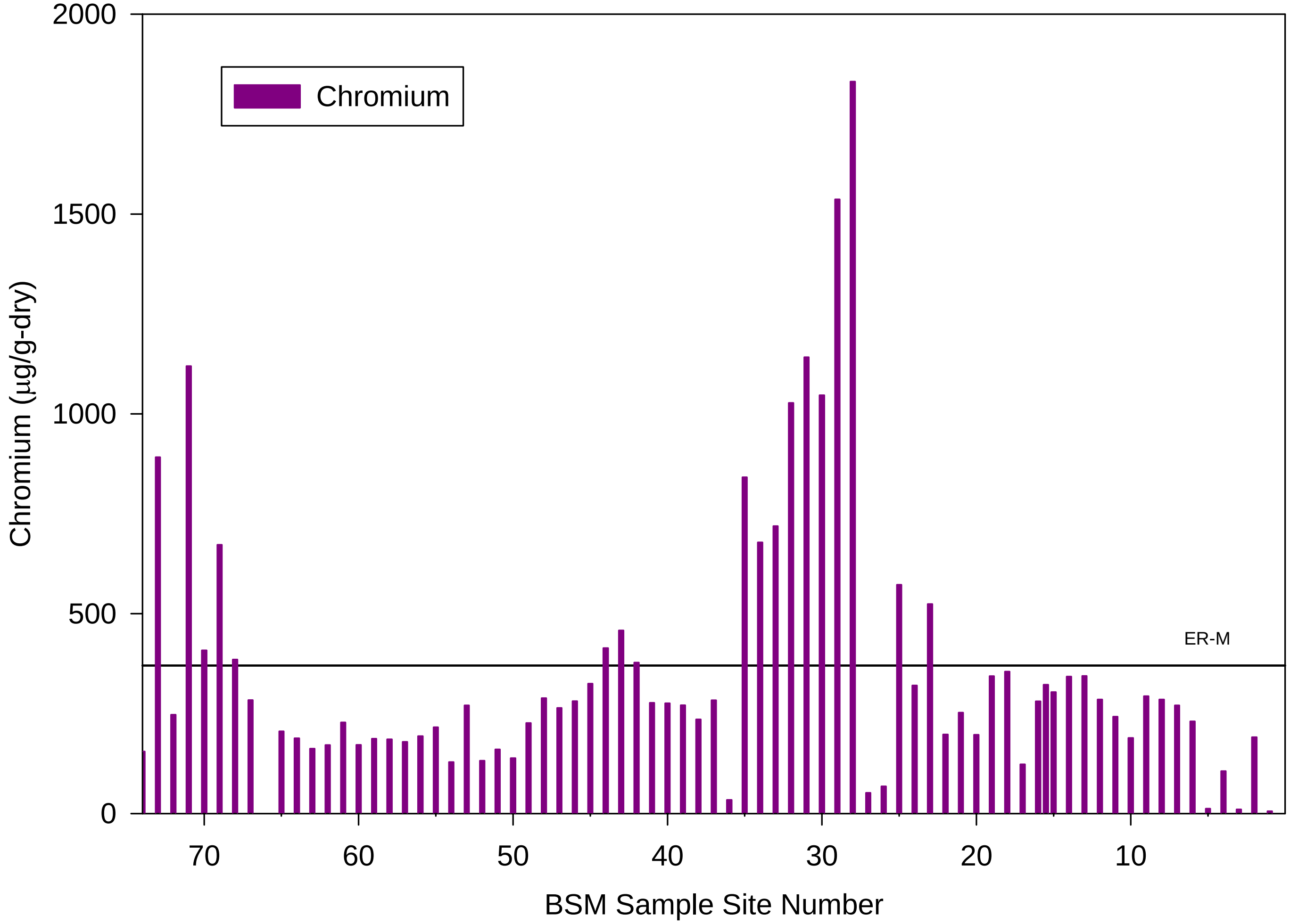
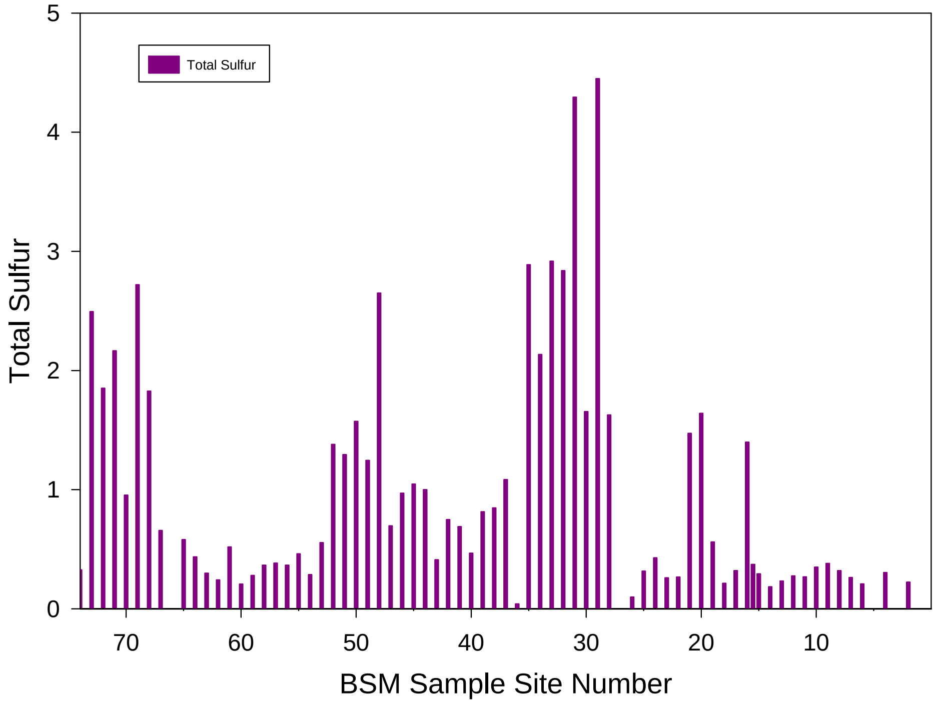
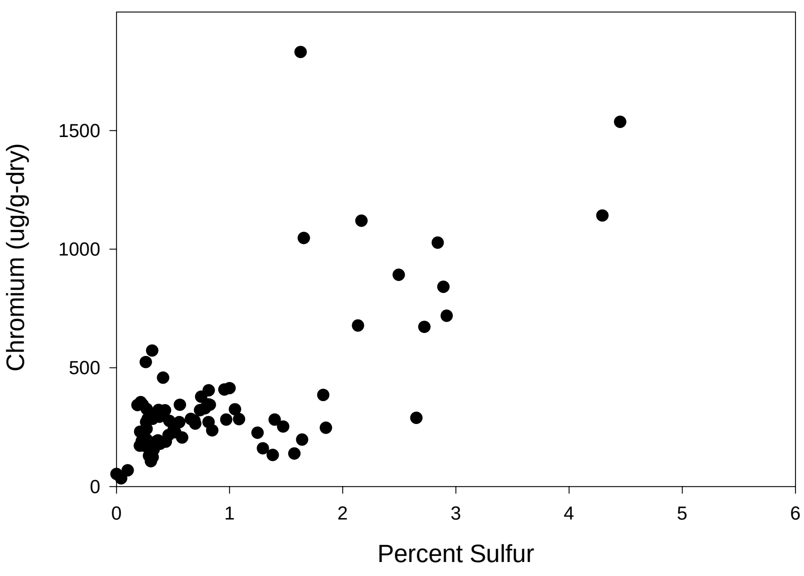


Baltimore Sediment Mapping Results: Correlation between metals and sulfur





August 2003 Chromium Speciation Study
Inner Harbor and Bear Creek

- Solid phase metals concentrations. Levels of chromium, copper, lead, and zinc exceed the 'effects range-median' in every sediment sample collected in this study. Cadmium levels exceeded ERM in five of the 12 Baltimore Harbor sites. No site exceeded the arsenic ERM.

- Concentrations of arsenic, cadmium, chromium, lead, and zinc in porewater did not exceed the most conservative water quality criteria in any of the samples in this study.

- Sediment porewaters are enriched in dissolved (filtrate) lead, chromium, and arsenic relative to the overlying waters, suggesting the potential for diffusional release of these metals from the sediments. Cadmium and zinc levels in pore waters are less than those in overlying waters.

- On average, one third of the solid phase chromium in the sampled Baltimore Harbor sediments is associated with acid-volatile sulfide, as determined by the AVS/SEM method.

- The acid-volatile sulfide concentrations exceed the total molar metals concentrations in the sediments, suggesting excess metal-binding capacity in these highly sulfidic sediments. This is consistent with the observation above of relatively low porewater metal levels surrounding solid phase sediments with high total metal levels (*e.g.*, sediments above ERM but porewater below WQC).

Temporal Trends

- Sediment cores: decadal changes

- Comparing among literature values: 1981, 1996, and 2003.

Metal Accumulation in Baltimore Harbor: Current and Past Inputs

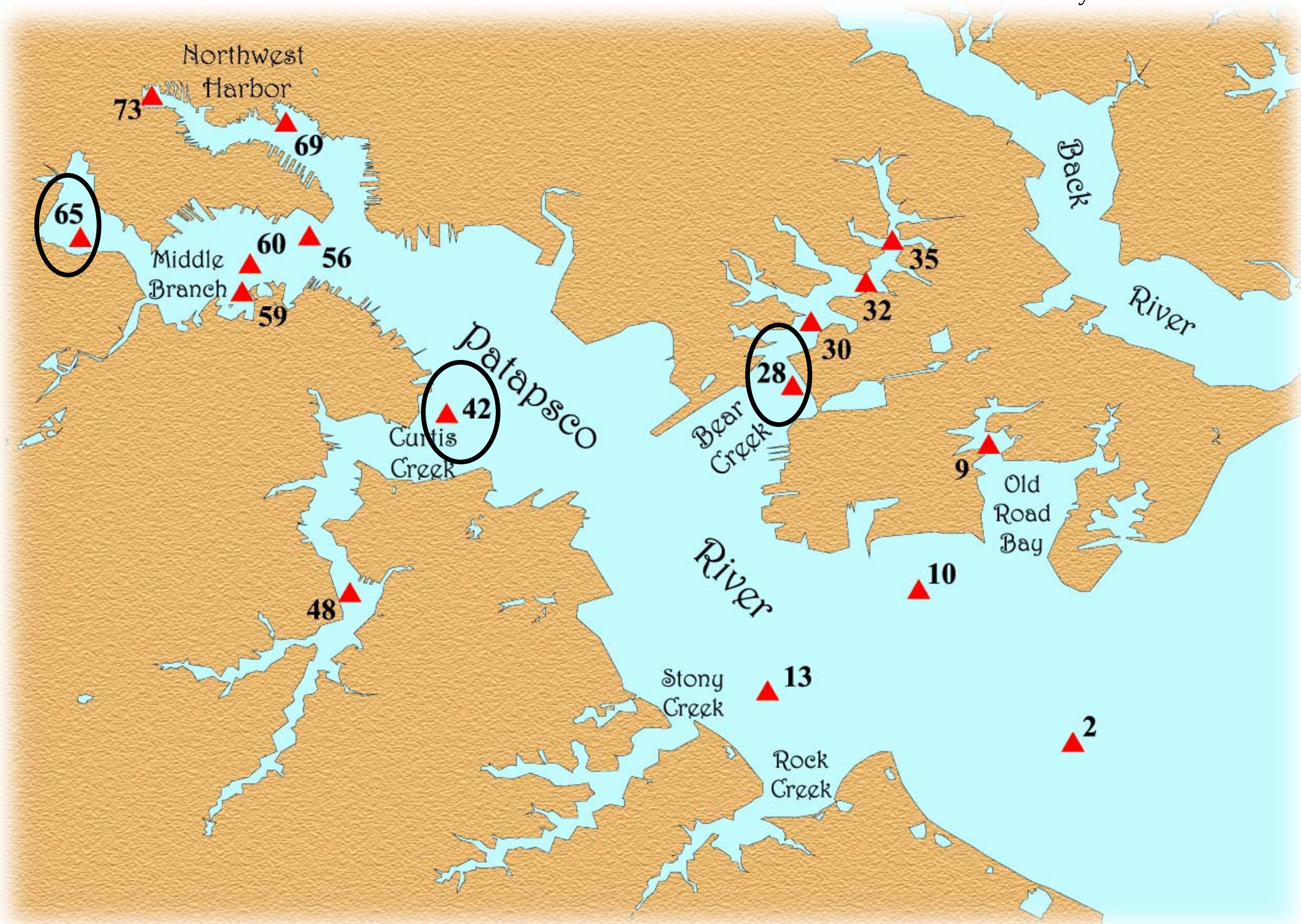
Robert P Mason*, Eun-Hee Kim and Jeffery Cornwell

Chesapeake Biological Laboratory, University of Maryland Center for Environmental Science (UMCES), PO Box 38, Solomons, MD 20688 and
Horn Point Laboratory, UMCES, Cambridge, MD.

Applied Geochemistry, in press

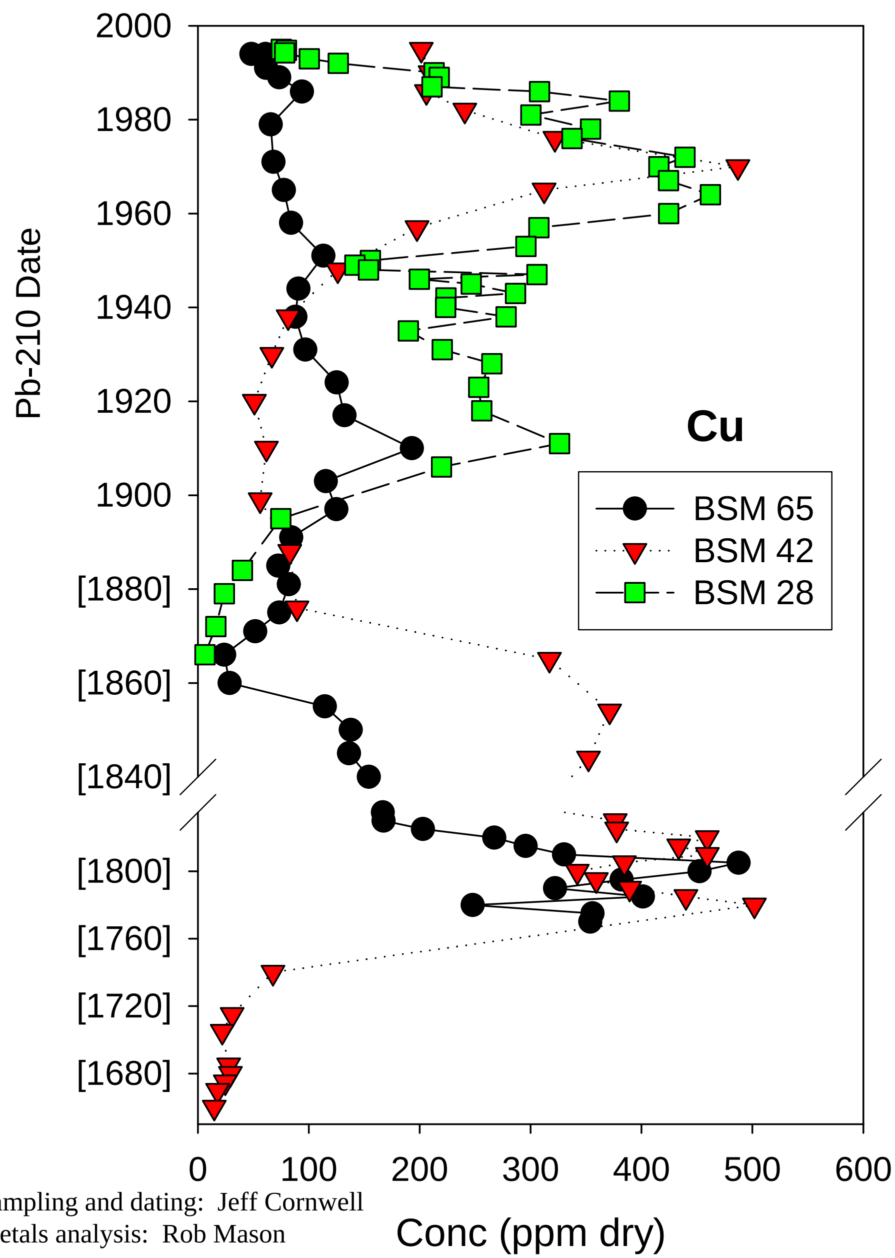
- Sediment cores from 3 locations in Baltimore Harbor
- Rate of sediment accumulation determined by Pb-210 dating
- Age of each sediment layer estimated
- Sediment layers analyzed for trace metals, organic carbon
- Temporal profiles compared to history of activities in the watershed

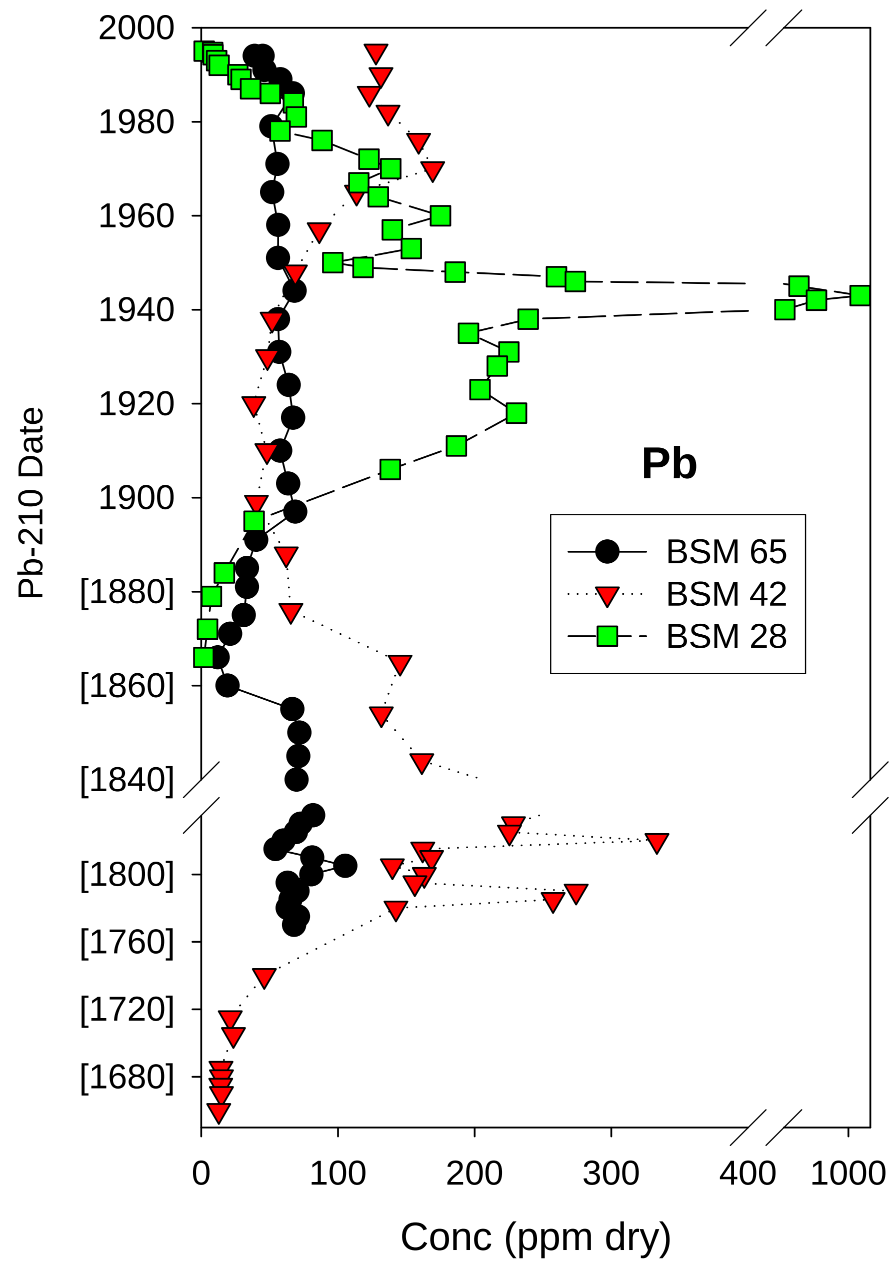
Sampling and dating: Jeff Cornwell
Metals analysis: Rob Mason



Sites from where deep cores were analyzed for metals

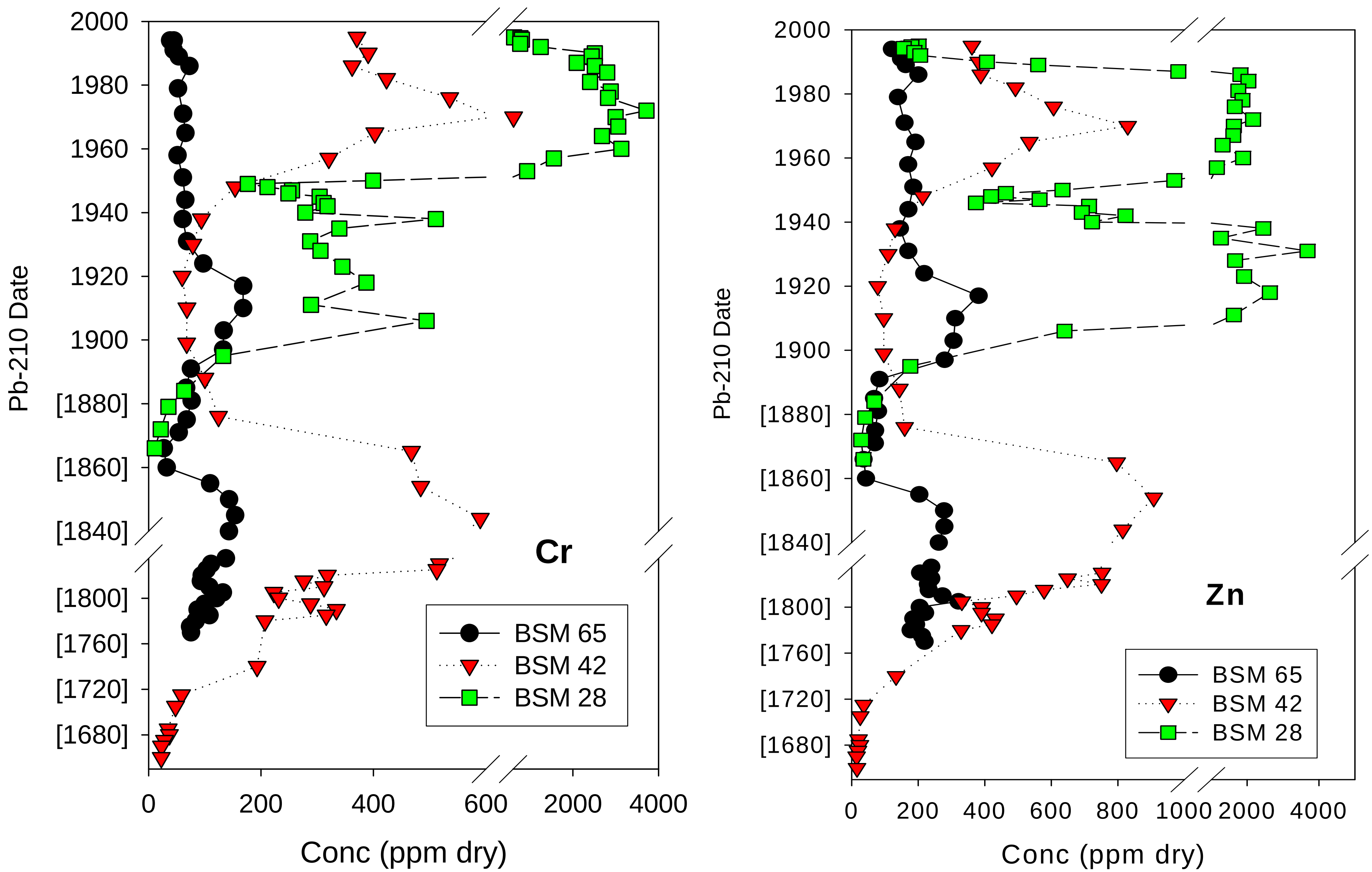
Both Cu and Pb high at Site 28 in 1900's. Cu also high at Sites 42 and 65 in 1800's. Profiles show differences. Metal content low in the pre-European era.





Sampling and dating: Jeff Cornwell
Metals analysis: Rob Mason

Profiles of Cr and Zn have some similarity over time. Again, high at Site 42 in the 1800's. Highest concentrations at Site 28 in the mid-1900's.



Sampling and dating: Jeff Cornwell
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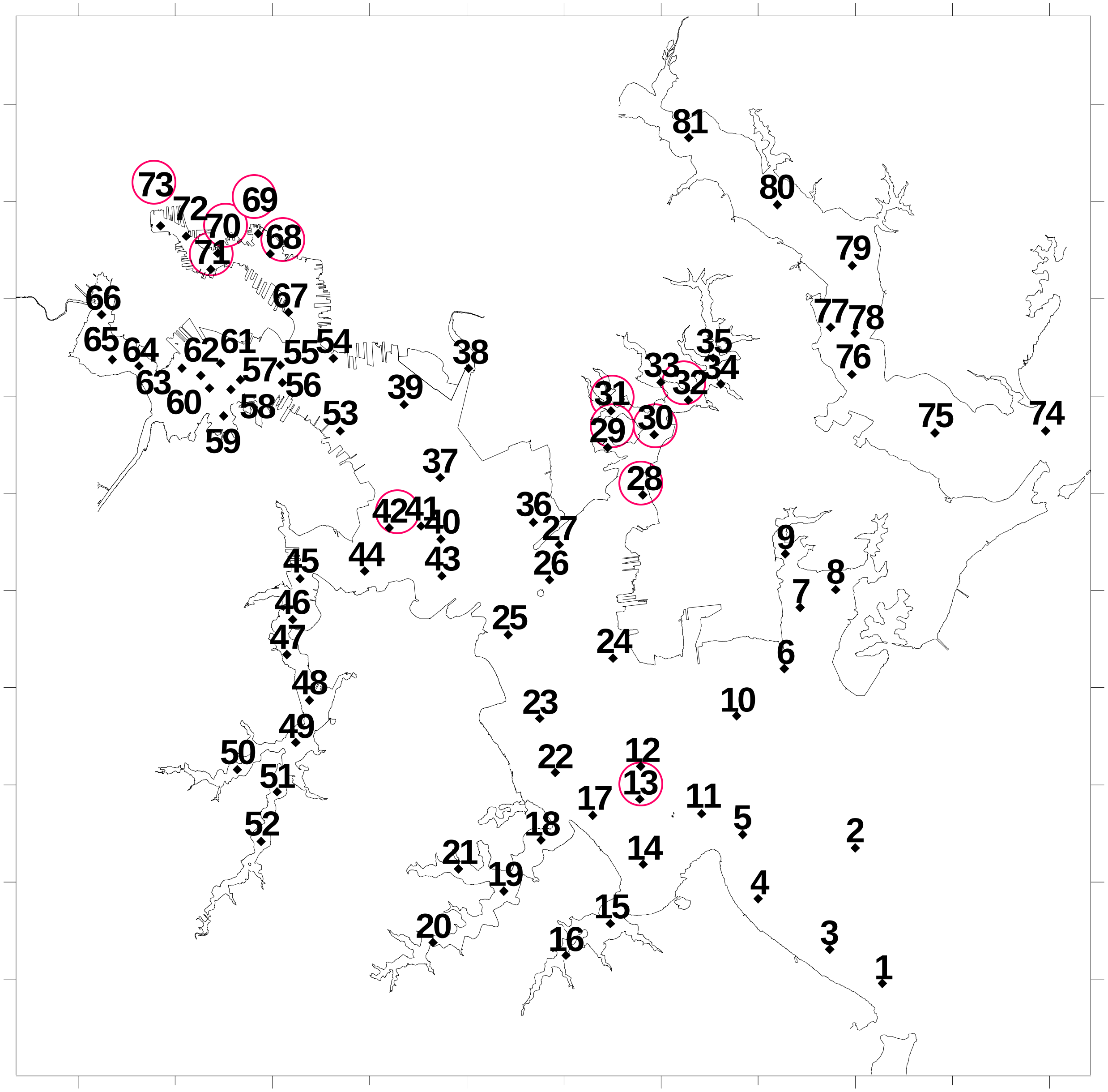
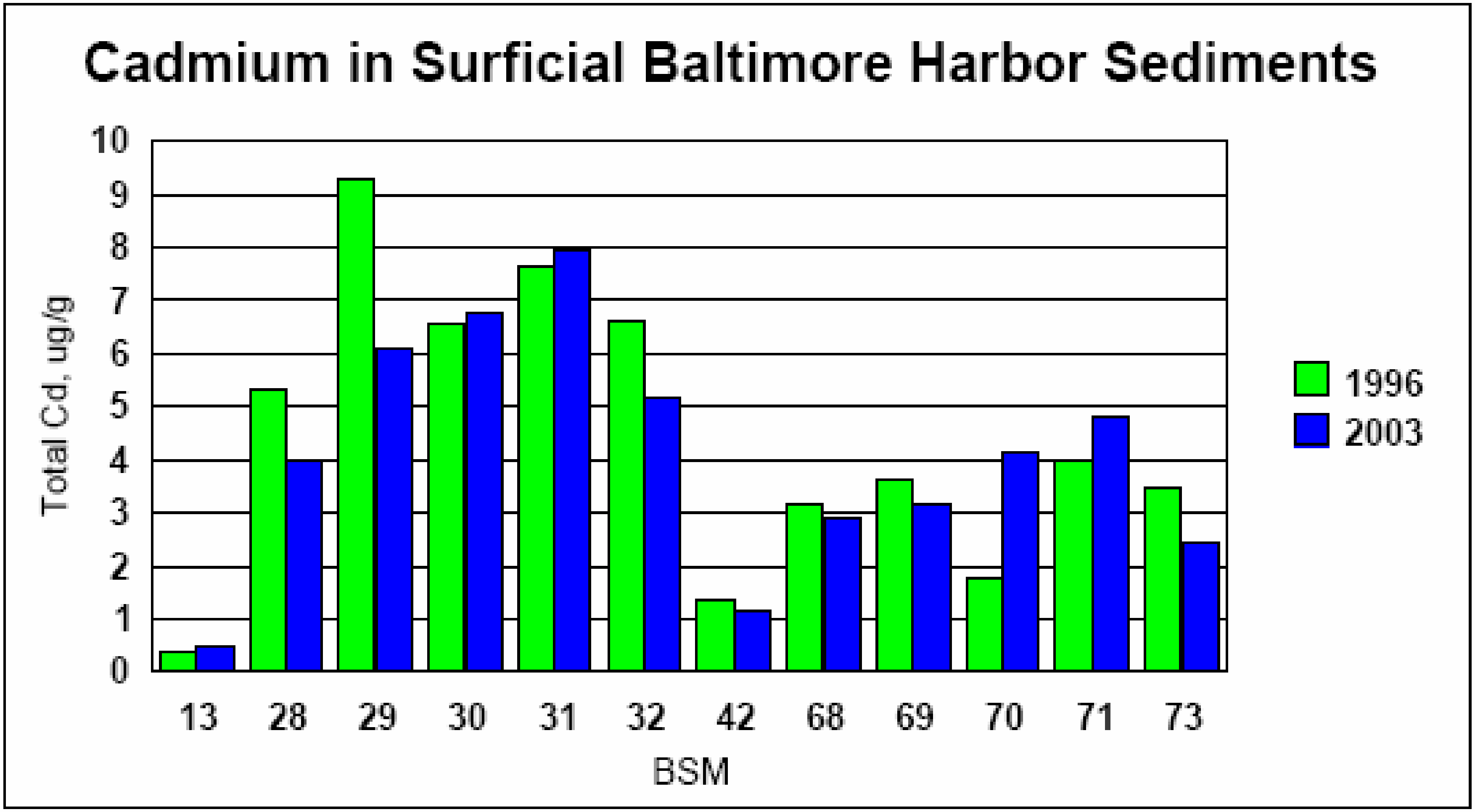
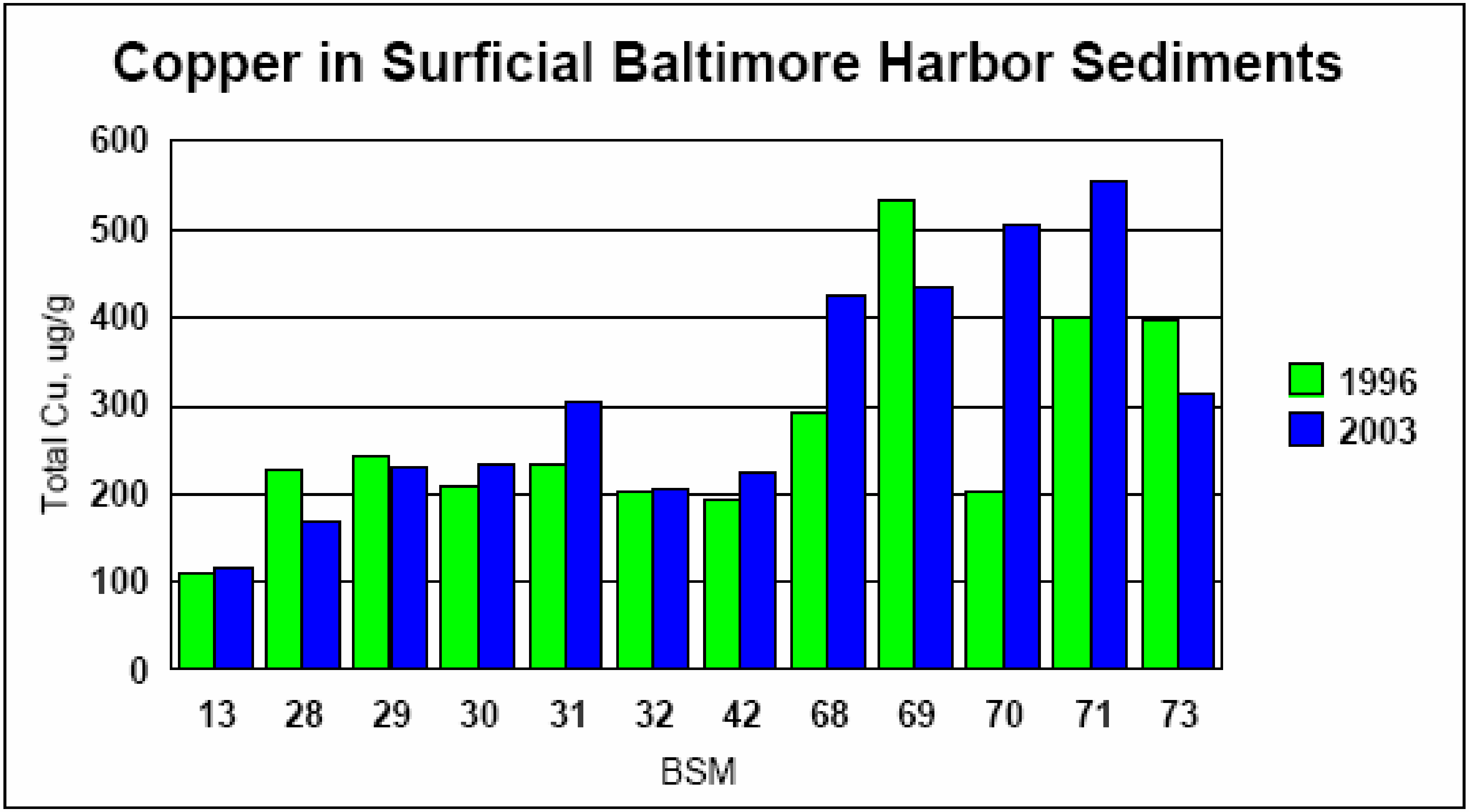
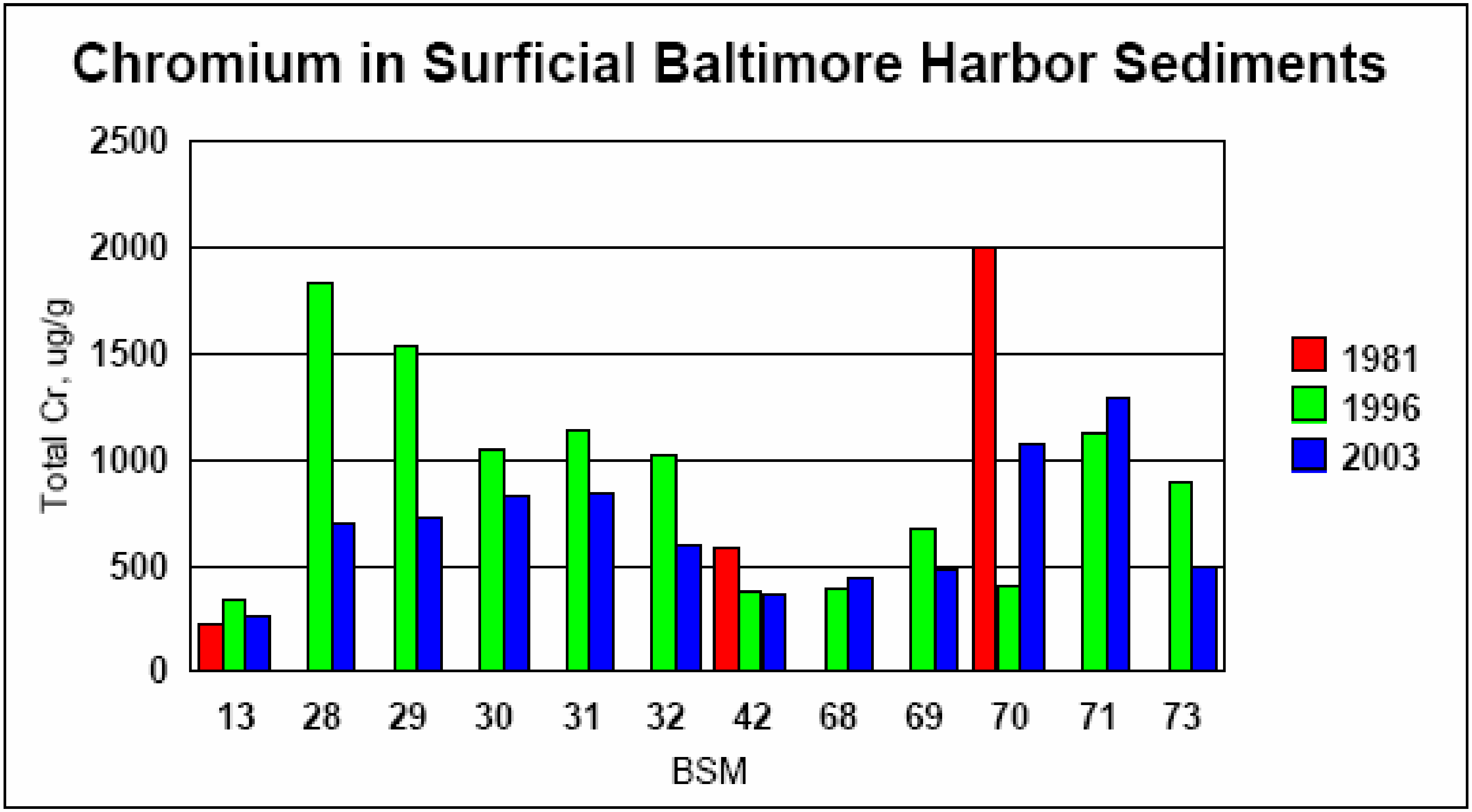
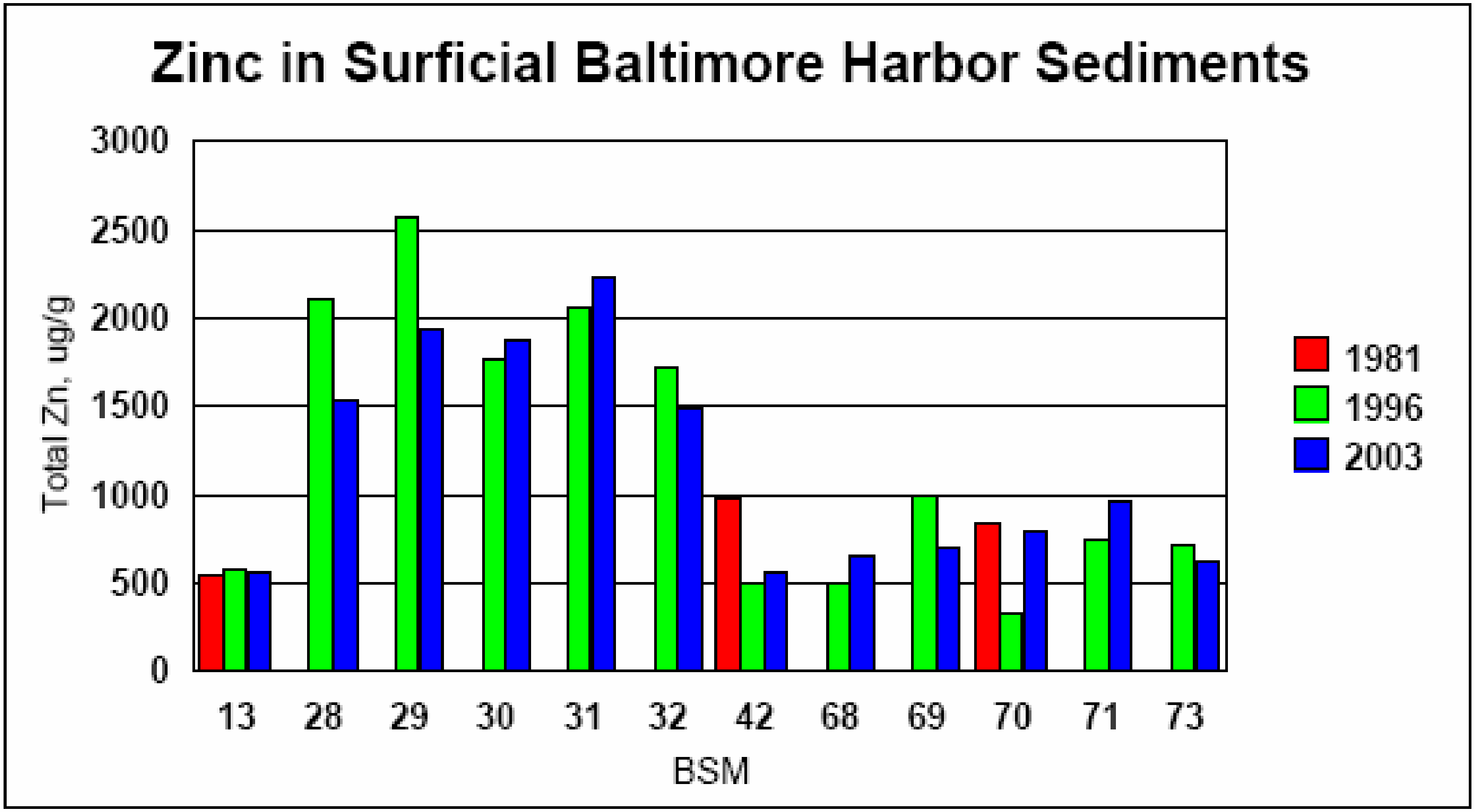
Baltimore Harbor Sediment Mapping (BSM) Stations




Cadmium in Surficial Baltimore Harbor Sediments
10
9
8
7
6
5
4
3
2
1
0
Total Cd, ug/g
13
28
29
30
31
32
42
68
69
70
71
73
BSM
1996
2003


Copper in Surficial Baltimore Harbor Sediments
Total Cu, ug/g
0
100
200
300
400
500
600
13
28
29
30
31
32
42
68
69
70
71
73
BSM
1996
2003


Chromium in Surficial Baltimore Harbor Sediments
2500
2000
1500
1000
500
0
Total Cr, ug/g
13
28
29
30
31
32
42
68
69
70
71
73
BSM
1981
1996
2003



Zinc in Surficial Baltimore Harbor Sediments
Total Zn, ug/g
3000
2500
2000
1500
1000
500
0
13
28
29
30
31
32
42
68
69
70
71
73
BSM
1981
1996
2003

Preliminary Observations

- There are no systematic trends in any of the 5 metals at the Outer Harbor site.
- Concentrations of chromium appear to have decreased between 1996 and 2003 at the Bear Creek station, with the largest apparent decline near the mouth of the creek.
- Chromium concentrations at site 70 appear to have declined after 1981, but chromium levels in other Inner Harbor sediments have not changed as dramatically.

Preliminary Observations (continued)

- Concentrations of copper are relatively invariant at the Bear Creek, Outer Harbor, and Curtis Creek sites, and more variable between 1996 and 2003 in the Inner Harbor stations.

- Cadmium levels are relatively invariant between 1996 and 2003, with perhaps a decline at stations 28 and 29 near the mouth of Bear Creek.

- Zinc levels are invariant at the Outer Harbor site (13) between 1981 and 2003, show no consistent trends in the Inner Harbor stations, and may have decreased slightly in Curtis Bay ant at the mouth of Bear Creek.

Toxicity Review